Sulfate-rich crustal fluids and REE tranpsort

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The presence of sulfate-rich fluids in natural magmatic hydrothermal systems and some carbonatite-related rare earth element (REE) deposits is paradoxical, because sulfate salts are known for their retrograde solubility, implying that they should be insoluble in hightemperature geofluids.

In our recent hydrothermal diamond anvil cell (HDAC) experiments in the Na_2SO_4-SiO_2-H_2O and Na_2SO_4-$Nd_2(SO_4)_3$-SiO_2-H_2O systems, we simulated the high-temperature behaviors of sulfate in the presence of excess quartz [1]. Sulfate-oversaturated systems are prepared at room temperature, by loading sulfate crystals, sulfated-satureated aqueous solution, and a quartz piece as starting materials. The experiment was conducted from room temperature to ~550 °C.

In the Na_2SO_4-SiO_2-H_2O system, the experiemnts show that the presence of quartz can significantly change the dissolution behavior of Na_2SO_4, leading to the formation of extremely sulfate-rich fluids (at least 42.8 wt% Na_2SO_4) at temperatures >~330 °C. The elevated Na_2SO_4 solubility results from prograde dissolution of immiscible sulfate melt, the water-saturated solidus of which decreases from ⩾ ~450 °C in the binary Na_2SO_4-H_2O system to ~270 °C in the presence of silica. Similar results were observed in the Na_2SO_4-$Nd_2(SO_4)_3$-SiO_2-H_2O system, and prograde dissolution of the Na-Nd-sulfate melting leaded to the formation an extremly Nd- and sulfate-rich fluid at ~420 °C.

These findings imply that sulfate-rich fluids should be common in quartz-saturated crustal environments and can be effective medium for REE mobilization.

[1] Cui, H. *et al*. (2020), *Geology* 48, 145–148.